Coordination of Strong Field Bidentate and Tridentate 1,2,4- Triazine Derivatives

H.A. Goodwin and F.E. Smith*

The preparation of iron(II), cobalt(II) and nickel (II) complexes of 3-(2-pyridyl)-5,6-diphenyl-1, 2, 4-triazine and 3-(2-(1,10-phenanthrolyl)-5,6-diphenyl-1, 2, 4, triazine is described. The former base acts a bidentate and the latter as a tridentate chelating agent. Both ligands produce a strong field and effect spin-pairing in iron(II). The magnetic properties of the cobalt (II) complexes show an anomalous temperature-dependence associated with a gradual, temperature- induced change in the spin-state of the cobalt atom. From the electronic spectra of the nickel(II) complexes estimates of the field strengths of the bases are obtained and the relationship between these and the ability to effect spinpairing in cobalt(II) is considered.

Introduction

There are numerous examples of bidentate and tridentate chelating agents containing heterocyclic donor nitrogen atoms in highly conjugated molecules which effect spin-pairing in iron(II).[1,2] Others have been shown to induce a temperature-dependent transition from the high-spin to the low-spin configuration in iron(II)[3] and there are also such molecules which, generally for steric reasons, give high-spin iron(II) complexes. Of the tridentate molecules which cause spin-pairing in iron(II) a large proportion produce an electronic equilibrium in cobalt(II).[3] This effect has been studied most extensively for what may be regarded as the parent tridentate of this class, 2,2',2"-terpyridine.[4,5,6] In the present work this relationship between the electronic configurations of iron(II) and cobalt(II) is explored further by a study of the complexes of the chelating agents 3-(2-pyridyl)-
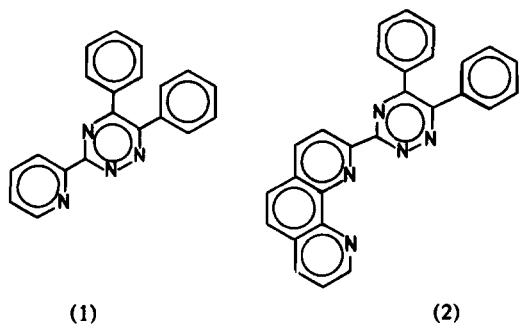

(1)   (2)

(*) Present adress: School of Chemcal Sciences, University of Penang, Minden, Penang, Malaysia.

5,6-diphenyl-1,2,4-triazine (1) (L₁) and 3-(2-(1,10-phenanthroly)-5,6-diphenyl-1, 2, 4-triazine (2) (L₂). These molecules are closely related to 2,2'-bipyridine and 2,2',2"-terpyridine, respectively, and might be expected to yield complexes with properties similar to those of complexes of the latter ligands. The presence of the two phenyl groups in (1) and (2) should not introduce any significant steric barrier to the coordination of these bases, provided that the nitrogen atoms in the 2-position of the triazine rings coordinate.

Results and Discussion

Compound (1) is one of a number of 1,2,4-triazines which have been prepared by Case[7] and whose analytical applications have been investigated by Schilt.[8] Compound (2) has not previously been reported, although Case described the closely related compound containing 2-pyridyl groups in place of phenyl groups attached to the triazine ring. Reaction of 1,10-phenanthroline-2-hydrazidine with benzil according to the general method of Case led to the formation of (2) which was obtained as a monohydrate.

Complexes of (1). Interaction of (1) with an ethanolic solution of the appropriate metal fluoroborate led to the separation of the tris-ligand complexes $[M(L_1)_3](BF_4)_2$ (M = Fe, Co, Ni). A strong tendency to form *bis*-ligand complexes with cobalt(II) necessitated the use of excess ligand in the preparation of $[Co(L_1)_3](BF_4)_2$. Failure to do this led to the formation of $[Co(L_1)_2(H_2O)_2](BF_4)_2$. When cobalt(II) salts containing coordinating anions were used *bis*-ligand complexes only were obtained.

The *tris*-ligand complexes all are bi-univalent electrolytes in nitromethane solution and their infrared spectra showed strong broad absorption at *ca.* 1050 cm⁻¹, indicative of uncoordinated tetrafluoroborate. The complexes are thus six-coordinate. Conductivity, room-temperature magnetic and analytical data

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Table I. Complexes of (1) (L₁) and (2) (L₂).

Compound	C Calc.	C Fd.	H Calc.	H Fd.	N Calc.	N Fd.	M Calc.	M Fd.	Λ* ohms⁻¹ cm²	μ (B.M.)(298K)
[Fe(L₁)₃](BF₄)₂ . 2H₂O	60.2	60.3	3.9	3.8	14.1	14.3	4.7	4.8	165	0.6
[Co(L₁)₃](BF₄)₂ . H₂O	61.0	61.0	3.8	3.8	14.2	13.7	5.0	5.1	165	3.3
[Ni(L₁)₃](BF₄)₂ . 3H₂O	59.2	59.6	4.0	3.8	13.8	14.3	4.8	4.7	158	3.3
[Co(L₁)₂(H₂O)₂](BF₄)₂	54.0	53.7	3.6	4.1	12.6	12.5	6.6	6.5	160	4.6
[Fe(L₂)₂](BF₄)₂ . 4H₂O	57.7	57.5	3.8	3.6	12.5	12.3	5.0	5.1	158	0.6
[Fe(L₂)₂]I₂ . 4H₄O	53.8	54.2	3.5	3.4	11.6	11.6	4.6	4.4	162	0.6
[Co(L₂)₂]Br₂ . 3H₂O	59.2	59.2	3.7	3.7	12.8	12.4	5.4	5.6	158	2.6
[Co(L₂)₂](BF₄)₂ . 3H₂O	58.5	58.8	3.6	3.6	12.6	12.3	5.3	5.6	161	4.4
[Co(L₂)₂](NO₃)₂ . 3H₂O	61.2	60.8	3.8	4.0	15.9	15.6	5.6	5.5	161	3.0
[Ni(L₂)₂](BF₄)₂ · 3H₂O	58.5	58.4	3.6	3.6	12.6	12.5	5.3	5.6	162	3.3

* Conductivity of $10^{-3}M$ solution in nitromethane at 298K.

Table II. Magnetic data for Co^{II} complexes. (Molar susceptibilities (x_M) incorporate diamagnetic corrections (Δ)).

T (K)	$10^6 x_M$	μ (B.M.)
[Co(L₁)₃](BF₄)₂ . H₂O		$(\Delta = -606 \times 10^{-6})$
83	8720	2.42
113	6740	2.48
143	5730	2.57
173	5220	2.70
203	4890	2.83
233	4800	3.0
273	4620	3.19
303	4680	3.38
323	4680	3.49
343	4650	3.59
363	4620	3.67
383	4590	3.77
[Co(L₂)₂](NO₃)₂ . 3H₂O		$(\Delta = -601 \times 10^{-6})$
83	8880	2.44
123	5990	2.44
173	4610	2.53
203	4160	2.61
233	3900	2.71
273	3720	2.86
303	3810	3.05
333	3990	3.27
[Co(L₂)₂](BF₄)₂ . 3H₂O		$(\Delta = -611 \times 10^{-6})$
83	27040	4.25
133	17440	4.33
173	13460	4.33
193	12090	4.34
243	9620	4.34
303	7790	4.36
[Co(L₂)₂]Br₂ . 3H₂O		$(\Delta = -632 \times 10^{-6})$
83	5910	1.99
123	3970	1.99
173	3040	2.06
233	2370	2.11
253	2340	2.18
273	2540	2.36
303	2800	2.62
323	3070	2.83
333	3100	2.89

being of greater intensity and undoubtedly due to a $t_2 \rightarrow \pi^*$ charge-transfer transition.[1]
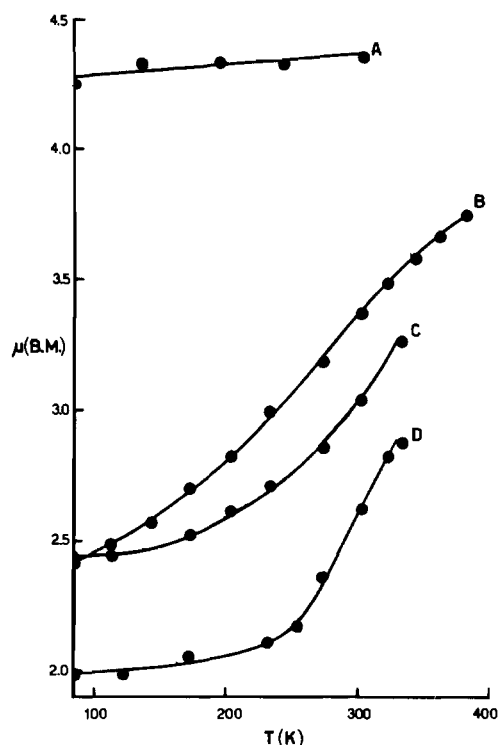
Figure 1. Magnetism of salts of $[Co(L_1)_3]^{2+}$ and $[Co(L_2)_2]^{2+}$. A. $[Co(L_2)_2](BF_4)_2$; B. $[Co(L_1)_3](BF_4)_2$; C. $[Co(L_2)_2](NO_3)_2$; D. $[Co(L_2)_2]Br_2$.

Although the properties of the iron(II) complex clearly indicate that it is low-spin, the magnetic moment for the cobalt(II) complex falls between the values expected for the metal in low-spin and high-spin configurations. Moreover the temperature- dependence of the magnetism reveals a marked deviation from Curie-Weiss behaviour. Detailed magnetic data are listed in Table 2 and the variation of magnetic moment with temperature is displayed in Figure 1. Within the experimental temperature range the moment varies smoothly from 2.4 B.M. at 83K to 3.8 B.M. at 383K. This variation is reversible and is reproduced by an independently prepared sample. It is obvious from Figure 1 that at the upper limit of the temperature range the moment has not reached its

for the complexes are collected in Table I. The deep purple iron(II) salt is essentially diamagnetic. The small moment observed is normal for low-spin iron (II) in similar complexes.[9] The diffuse reflectance spectrum of the complex shows two intense and broad absorptions at 19200 and 11600cm⁻¹, the former

(9) E. König and S. Kremer, *Theor. Chim. Acta*, 22, 45 (1971).

maximum value but loss of water of hydration and decomposition of the complex at more elevated temperatures precluded extending the range. The behaviour of this complex is similar to that observed for a number of other cobalt(II) complexes derived from bidentate and tridentate chelating agents related to (1).[4,10,11] As in those instances, the most likely explanation for the anomalous behaviour is a smooth transition from the low-spin (^2E) state to the high-spin ($^4T_1$) in the metal atom, implying that the strength of the field produced by (1) lies very close to the crossover value for cobalt(II). A quantitative estimate of the field strength of (1), when coordinated to Co^{II}, could not be obtained from the electronic spectrum of the complex since this is dominated by an intense charge-transfer absorption leading in from the ultra-violet and displaying two broad shoulders centred at about 20900 and 13000 cm^{-1}, a pattern fairly typical for this class of compound. The spectrum of the corresponding nickel(II) complex [Ni(L₁)₃](BF₄)₂ allows a reasonable estimate for Dq(Ni^{2+}) to be made. The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is observed at 12750cm⁻¹, indicating a value of 1275 cm⁻¹ for Dq(Ni^{2+}). This is very close to the range expected for this class of ligand[4,12] and indeed is almost identical to the value obtained[13] for 1,10-phenanthroline.

The tris(1,10-phenanthroline)cobalt(II) ion is high-spin but the temperature-dependence of the magnetism of only one salt, the perchlorate, has been reported,[14] and this follows a normal Curie-Weiss law. In view of the close relationships between (1) and 1,10-phenanthroline and of the marked counterion dependence of the magnetism of complex cations in which a spin-transition occurs[10,15,16] it was considered worthwhile to investigate the [Co(phen)₃]²⁺ system further by the isolation and study of additional salts. The temperature-dependence of the magnetism of the tetrafluoroborate, nitrate, iodide and bromide in each instance followed the Curie-Weiss law $xM = C/T-\theta$ with small θ values (listed in Table III) over the range 83-289K. Thus, although (1) and phenanthroline produce an almost equivalent field strength about nickel(II), phenanthroline, unlike (1), is not able to effect spin-pairing in cobalt(II). This difference may result from small differences in the symmetry of the environment about the cobalt atom in complexes of the two ligands, due either to intrinsic differences in the

ligands or to packing effects in the solids.

Complexes of (2). The tridentate phenanthroline derivative (2) yields complexes with properties similar to those of the pyridine derivative (1). Thus *bis*-ligand complexes [M(L₂)₂]X₂ were isolated with iron (II), cobalt(II) and nickel(II). These were all found to be bi-univalent electrolytes in nitromethane (Table I) and are normal six-coordinate complexes with each molecule of (2) coordinating as a tridentate chelate group with the three donor nitrogen atoms necessarily occupying an equatorial plane of the coordination octahedron because of the rigidity of the phenanthroline nucleus.

The deep purple *bis*-ligand iron(II) salts were found to have very low magnetic moments, characteristic of the metal atom in an essentially pure $^1A_1$ state. The diffuse reflectance spectrum of [Fe(L₂)₂]-(BF₄)₂ reveals strong charge-transfer absorption extending almost right across the visible region with prominent peaks at about 14000 and 20000 cm^{-1}. In the spectrum of a solution of the complex the charge-transfer absorption, arising from $t_2 \rightarrow \pi^*$ transitions, is resolved into two clear peaks at 15300 and 20200cm⁻¹ (figure 2). The band at lower frequency
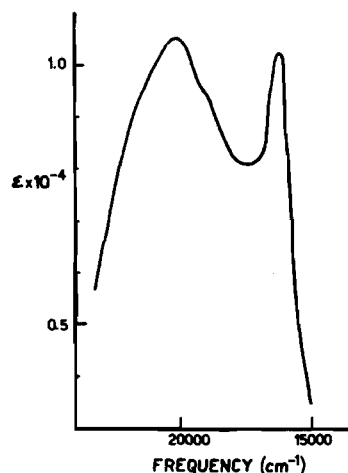

Figure 2. Electronic spectrum of [Fe(L₂)₂](BF₄)₂ (M/5000 solution in dimethylformamide).

is the more narrow, as is characteristically found for the "iron(II)-bis-terimine" system[17], and there is, again typically, a weak shoulder on the lower frequency side of the main absorption peak.

The dark brown *bis-ligand* cobalt(II) salts were found to have magnetic properties characteristic of a crossover system. The detailed magnetic data are listed in Table II and plots of magnetic moments *vs.* temperature are shown in Figure 1. The tetrafluoroborate salt was found to behave as a simple paramagnetic substance, but with a magnetic moment (4.4 B.M. at 303K) slightly lower than that normally encountered for high-spin, six-coordinate cobalt(II). The nitrate and bromide salts, however, showed marked deviation from Curie-Weiss behaviour. At low temperatures the magnetic moments of these two compounds approach the value expected for low-spin

Table III. Magnetsm of salts of [Co(phen)₃]²⁺.

Salt	μ (83K) (B.M.)	μ (289K) (B.M.)	θ (K)
iodide	4.4	4.8	−22
bromide	4.3	4.7	−22
tetrafluoroborate	4.4	4.7	−22
nitrate	4.7	5.0	−10

(10) H.A. Goodwin, R.N. Sylva, R.S. Vagg, and E.C. Watton, *Austral. J. Chem.*, 22, 1605 (1969)
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(17) P. Krumholz, *Inorg. Chem.*, 4 612 (1965).

cobalt(II). As the temperature is increased a Curie-Weiss law is followed to just beyond 100K where marked deviation from Curie-Weiss behaviour occurs. It would seem from the plots in Figure 1 that the lower limit of the magnetic moment for the nitrate is about 0.5 B.M. greater than that for the bromide indicating that in the nitrate salt there is a certain proportion of complex ions which do not take part in the spin transition but remain permanently in the $^4T_1$ state. This contribution of permanently high-spin ions to the "residual" magnetism is a feature characteristic of crossover systems and is particularly common in such iron(II) complexes.[18,19] The different behaviours of the three salts of $[Co(L_2)_2]^{2+}$ were reproduced for independently prepared samples. The anomalous magnetism of these salts closely parrallels that observed in related systems and in $[Co(L_1)_3](BF_4)_2$. The influence of the counter anion is seen to be quite profound and presumably has its origins in small variations in the symmetry of the environment about the metal atom, resulting from either electrostatic interactions between the complex cation and the anions, or from steric distortions due to different packing requirements for the different salts. The effect of these perturbations can be expected to be extremely significant in a crossover system, critically sensitive to small variations in ligand field strength.

The diffuse reflectance spectra of salts of $[Co(L_2)_2]^{2+}$ reveal two prominent shoulders to a strong charge-transfer absorption emerging from the ultraviolet. The broad pattern observed is very similar to that found for other cobalt(II)-tridentate imine systems,[5,10] but the spectra are not sufficiently well resolved to allow a reliable estimate of the ligand field parameters. Resolution in the spectra of solutions of the salts is little better and all the spectra are similar with shoulders to the charge-transfer band at about 21500 and 18200cm^{-1}. In the spectrum of $[Ni(L_2)_2]$-$(BF_4)_2$ the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is observed at 12120 cm^{-1} giving a $Dq(Ni^{2+})$ value of 1212 cm^{-1}, somewhat lower than that for (1) and for terpyridine[15] (1275 cm^{-1}). The lower value for the tridentate, as compared with the bidentate (1) probably arises from the bond angle distortions necessary to allow coordination of the three donor nitrogen atoms. Such distortions are present in complexes of terpyridine[20] but in complexes of (2) they could be expected to be less evenly distributed over the molecule because of the rigidity of the phenanthroline nucleus. The importance of the influence of low symmetry components in determining the magnetic properties of cobalt(II) systems such as those considered here has been emphasized by Judge and Baker[5], and it was earlier suggested[4] that the accessibility of the low-spin (^2E) state for cobalt in complexes containing imine-type ligands would be enhanced by a tetragonal distortion of the coordination octahedron.

It is apparently the phenanthroline rather than the triazine moiety in (2) which is responsible for its reduced field strength, compared with that of terpyridine, since the triazine system in (2) is also present in the bidentate (1) and the field strength of the latter is little altered from that of either phenanthroline or bipyridine. Despite this apparent reduction in field strength the tridentate (2) is still able to effect spin-pairing in cobalt(II) and in this regard the similar behaviour of both a bidentate and its tridentate derivative is unusual.

Experimental Section

Preparation of Ligands. The triazines (1) and (2) were prepared from the corresponding hydrazidines according to the general method of Case.[7] The pyridine derivative (L$_1$) was obtained as a yellow crystalline solid from ethanol. M.P. 190°C (lit.[7] 189-190°C). The phenanthroline derivative (L$_2$) was obtained as a yellow crystalline monohydrate from ethanol. M.P. 137°C. Its mass spectrum showed the expected parent ion peak at m/e = 411. *Anal.* Found: C, 74.9; H, 4.5; N, 16.3. Calcd. for $C_{27}H_{17}N_5 \cdot H_2O$: C, 75.5; H, 4.5; N, 16.3.

Complexes of (1). (a) $[M(L_1)_3](BF_4)_2$ (M = Fe, Ni). To a solution of (1) (0.93g, 3 mmole) in hot ethanol 30 ml) was added a solution of $M(BF_4)_2 \cdot 6H_2O$ (0.34g, 1 mmole) in ethanol (15 ml). The mixture was allowed to cool and the complex crystallised. It was washed with ethanol and dried *in vacuo.* (b) $[Co(L_1)_3](BF_4)_2$. In this instance the procedure followed was the same as for the complexes of Fe^{2+} and Ni^{+2} above, except that 1.24g (4 mmole) of (1) was used. Failure to use excess (1) resulted in the formation of the greenish-brown *bis*-ligand complex $[Co(L_1)_2$-$(H_2O)_2](BF_4)_2$.

Complexes of (2). With the exception of $[Fe$-$(L_2)_2]I_2$ all the metal complexes were prepared by the following procedure. To a hot solution of (2) (0.86g, 2 mmole) in ethanol (80 ml) was added a solution of the appropriate metal salt (1 mmole) in hot ethanol (20 ml). The solution was set aside to cool and the product crystallised. The complex was washed with ethanol and dried *in vacuo.*

$[Fe(L_2)_2]I_2$ was obtained by reaction of (2) (0.86g, 2 mmole) in ethanol (70 ml) with $FeCl_2 \cdot 4H_2O$ (0.4g, 2 mmole in ethanol (20 ml). Ether was added to the resultant deep purple solution when $[Fe(L_2)Cl_2]$ crystallised. This impure purple powder was dissolved in hot water and when sodium iodide was added the complex iodide crystallised. It was washed with water and dried *in vacuo.*

Magnetic measurements. Magnetic data were obtained using a Newport variable temperature Gouy balance. The magnetism of all samples was found to be independent of field strength at both the upper and lower limits of the experimental temperature range.

Electronic Spectra. Diffuse reflectance and solution spectra were obtained with a Zeiss PMQII spectrophotometer with RA3 reflectance attachment calibrated against magnesium oxide.

Analyses. Carbon hydrogen and nitrogen analyses were determined by Dr. E. Challen and Mr. J. Sussman, University of New South Wales. Metals were estimated gravimetrically.

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